

## Mid-Pliocene deep-sea bottom-water temperatures based on ostracode Mg/Ca ratios

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Received 9 August 2004; received in revised form 13 December 2004; accepted 13 December 2004

### Abstract

We studied magnesium:calcium (Mg/Ca) ratios in shells of the deep-sea ostracode genus *Krithe* from a short interval in the middle Pliocene between 3.29 and 2.97 Ma using deep-sea drilling sites in the North and South Atlantic in order to estimate bottom water temperatures (BWT) during a period of climatic warmth. Results from DSDP and ODP Sites 552A, 610A, 607, 658A, 659A, 661A and 704 for the period Ma reveal both depth and latitudinal gradients of mean Mg/Ca values. Shallower sites (552A, 610A and 607) have higher mean Mg/Ca ratios (10.3, 9.7, 10.1 mmol/mol) than deeper sites (661A, 6.3 mmol/mol), and high latitude North Atlantic sites (552A, 610 and 607) have higher Mg/Ca ratios than low latitude (658A: 9.8 mmol/mol, 659A: 7.7 mmol/mol, 661A: 6.3 mmol/mol) and Southern Ocean (704: 8.0 mmol/mol) sites. Converting Mg/Ca ratios into estimated temperatures using the calibration of Dwyer et al. (1995) [Dwyer, G.S., Cronin, T.M., Baker, P.A., Raymo, M.E., Buzas, J.S., Corrège, T., 1995. North Atlantic deepwater temperature change during late Pliocene and late Quaternary climatic cycles. *Science* 270, 1347–1351] suggests that mean middle Pliocene bottom water temperatures at the study sites in the deep Atlantic were about the same as modern temperatures. However, brief pulses of elevated BWT occurred several times between 3.29 and 2.97 Ma in both the North and South Atlantic Ocean suggesting short-term changes in deep ocean circulation. Published by Elsevier B.V.

**Keywords:** Paleoceanography; Pliocene; ostracode shell chemistry; ocean temperature; Mg/Ca

### 1. Introduction

Much of the Pliocene period is characterized by relative climatic warmth (Dowsett et al., 1996), low amplitude climate cycles (compared to cycles of the late Quaternary) (Raymo et al., 1989, 1990, 1992;

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Shackleton et al., 1995), high eustatic sea level (Dowsett and Cronin, 1989; Kennett and Hodell, 1993), strong North Atlantic Deep Water (NADW) formation (Raymo et al., 1992; Raymo, 1994), greater equator-to-pole heat transport in the North Atlantic (Dowsett et al., 1992), warm continental climates around the North Atlantic (Willard, 1994), and reduced Arctic Ocean sea ice (Cronin et al., 1993).

Several direct or indirect factors, not mutually exclusive of one another, may have contributed to warm climates during at least some intervals in the early to middle Pliocene and the subsequent development of strong glacial–interglacial cycles after ~2.75 Ma (see Crowley, 1991; Sloan et al., 1996; Haug et al., 2001). These factors include high atmospheric CO<sub>2</sub> (Crowley, 1991; Kurschner et al., 1996; but see Pearson and Palmer, 2000; Demicco et al., 2003), changes in oceanic heat transport (Rind and Chandler, 1991; Dowsett et al., 1992), lowered Arctic Ocean sea ice (Raymo et al., 1990; Crowley et al., 1994), the closing of the Indonesian seaway and development of a long-term El Niño climate state (Cane and Molnar, 2001; Molnar and Cane, 2002), and the emergence of the central American Isthmus (Keigwin, 1982; Cronin, 1988; Cronin and Dowsett, 1996; Mikolajewicz and Crowley, 1997; Haug and Tiedemann, 1998; Haug et al., 2001). Raymo et al. (1996) characterized the Pliocene as having “stronger greenhouse and stronger conveyor”, in agreement with Dowsett et al. (1996), who also concluded that both enhanced equator-to-pole oceanic heat transport and higher atmospheric concentrations of carbon dioxide contributed to middle Pliocene warmth. However, more recent studies have emphasized the importance of closing of ocean gateways and atmospheric circulation (Haug and Tiedemann, 1998; Haug et al., 1999; Cane and Molnar, 2001; Billups et al., 1999).

The hypothesis that ocean circulation changes led to greater North Atlantic deep-water (NADW) formation contributing to Pliocene global warmth means that deep-sea bottom water temperatures (BWT) in the Atlantic Ocean may have been as warm or warmer than at present. Previous studies provide limited evidence for warm deep BWTs. Raymo et al. (1992) studied middle Pliocene stable isotopes from four deep-sea cores and postulated strong NADW production and either warmer BWTs or reduced Antarctic

ice, or both. Dwyer et al. (1995) found that Mg/Ca ratios in *Krithe* from Pliocene sediments at DSDP Site 607 suggest bottom water temperatures as high or slightly higher than those at that region today. Ishman (1996) and Cronin (1996) attributed benthic foraminiferal and ostracode faunal patterns in DSDP Sites 607 and 610A in the North Atlantic Ocean to large-scale changes in deep oceanic circulation near 3 Ma. In the Indian Ocean, Chen et al. (1995) compared benthic and planktonic foraminiferal isotope records from ODP Site 758 and concluded that deep-sea bottom water temperatures were unstable, but did not necessarily change in phase with maximum glaciations. For the period ~3.2–3.8 Ma they estimated BWT was about 0.5–1.0 °C cooler than modern temperatures at that site. Billups et al. (1998) concluded from isotopic records from the Ceara Rise that BWTs were ~0.6 to 1.5 °C warmer during the interval 4.2–3.7 Ma.

In this paper, we analyze Mg/Ca ratios of the ostracode genus *Krithe* and estimate bottom water temperatures in the deep Atlantic Ocean during the middle Pliocene, between about 3.0 and 3.3 Ma, the interval investigated in detail in the PRISM (Pliocene Research, Interpretation, and Synoptic Mapping) Project (Dowsett et al., 1994, 1996, 1999). Dwyer et al. (1995) used Mg/Ca paleothermometry of *Krithe* to provide the first quantitative evidence based on trace elemental analyses for oscillations in North Atlantic BWT during Late Pliocene and late Quaternary glacial–interglacial cycles. They gave preliminary evidence that at DSDP Site 607, middle Pliocene BWT averaged ~2.7 °C, which is approximately the modern temperature at the site. Bottom water temperature changes in the same region of the western Mid-Atlantic Ridge have also been documented during late Quaternary millennial scale Heinrich events (Cronin et al., 2000). These studies showed that on the western Mid-Atlantic Ridge, North Atlantic at depths of 3427 m late Pliocene 41-ky obliquity cycles experienced BWT excursions averaging 2.3 °C and late Quaternary 100-ky cycles varied by as much as 4 °C. Evidence for Late Quaternary BWT changes during glacial–interglacial cycles has since been verified using Mg/Ca ratios in the deep-sea foraminifera *Cibicidoides wuellerstorfi* from the equatorial Atlantic at depths of 3912 m (Martin et al., 2002).

## 2. Mg/Ca paleothermometry using ostracode shells

Biogenically (Chave, 1954) and inorganically precipitated (Oomori et al., 1987; Mucci, 1987; Burton and Walter, 1991) calcite incorporate amounts of magnesium that are often proportional to the temperature at the time of precipitation (see Morse and Mackenzie, 1990). Early studies of ostracode shell chemistry by Cadot et al. (1972, 1975) and Cadot and Kaesler (1977) used the electron microprobe to investigate several genera of marine ostracodes. They reached four important conclusions. First, they demonstrated significant variability in magnesium content in several ostracode superfamilies. For example, the genera *Argilloecia*, *Krithe*, and *Xestoleberis* had average magnesium concentrations of 6.3–8.3, 1.6, and 3.4–4.5 mole percent, respectively. Second, they showed different levels of variability in layers of the carapace of some taxa. Third, they inferred an ecologically adaptive advantage to discontinuous gradations in magnesium through the shell in some genera (see Swanson, 1995). Fourth, they demonstrated an apparent relationship between water temperature and magnesium content in several taxonomic groups, including the genus *Krithe* over a limited temperature range.

Chivas et al. (1983, 1986; De Deckker et al., 1988) pioneered efforts using trace elemental geochemistry (Mg, Sr) of non-marine, brackish, and shallow marine ostracodes to derive distribution coefficients for several genera (Chivas et al., 1993). Additional work on non-marine ostracode shell geochemistry and application to paleolimnology has been carried out by Engstrom and Nelson (1991); Holmes (1992); Holmes et al. (1992); Curtis and Hodell (1993); Palacios-Fest et al. (1993); Wansard (1996), Xia et al. (1997), and others.

The principles of applying shell chemistry to deep-sea taxa are similar to those for non-marine and estuarine taxa with two important differences. In contrast to estuarine ostracode shell chemistry where salinity variability can dominate the metal/calcium ratios (De Deckker et al., 1988; Dwyer et al., 2002), salinity variability is not a major factor in deep benthic habitats. Second, the first calibration equations relating ocean temperature to magnesium concentration in shells were derived from field studies of coretop specimens (Corrège, 1993;

Dwyer et al., 1995) rather than from culturing living populations.

The ubiquitous deep-sea genus *Krithe* has been the focus of most deep-sea ostracode shell chemistry. Corrège (1993), using atomic absorption (AA) spectrophotometry, showed a positive relationship between bottom water temperature and Mg/Ca in *Krithe* from the Coral Sea over water temperatures from 2 to 6 °C, generally confirming the results of Cadot and Kaesler (1977). Corrège (1993) was also able to apply his calibration to show reduced glacial-age BWT at Ocean Drilling Program (ODP) Site 822 in the Pacific Ocean. Dwyer et al. (1995) developed a more extensive calibration data set for *Krithe* and applied it to secular variation in *Krithe* Mg/Ca ratios from Pliocene and late Quaternary sediments from DSDP Site 607 and *Chain* core 82-24-4PC from the western flank of the mid-Atlantic Ridge, North Atlantic Ocean (3427 m water depth). Using primarily direct current plasma (DCP) emission spectrometry, they developed a provisional temperature-Mg/Ca calibration equation using modern coretop material from the Little Bahama Banks (Slowey and Curry, 1995) and elsewhere in the North Atlantic for bottom water temperatures ranging from 2 to 14 °C. They found approximately the same temperature Mg/Ca relationship as that derived by Cadot and Kaesler (1977) and by Corrège (1993) despite using *Krithe* from different areas and the use of different analytical techniques. Dwyer et al. (1995) applied the paleotemperature equation to estimate BWTs during late Pliocene 41-ky (3.2–2.4 Ma) and Quaternary 100-ky climatic cycles (oxygen isotope stages 6–1) and found that oscillations in Mg/Ca during Pliocene and Quaternary climatic cycles correlated with oxygen isotope and faunal patterns at this site (see also Cronin and Raymo, 1997; Cronin et al., 2000).

Cronin et al. (1996) studied intraspecific variation of Mg/Ca in *Krithe glacialis* and *K. minima* obtained for the Arctic Ocean and the Norwegian, Greenland, and Iceland (Nordic) Seas for bottom water temperatures ranging from –1.5 to +4 °C. They generally confirmed a positive Mg/Ca-temperature correlation for shallow-water *Krithe* that were living on the continental shelves of the Barents and Laptev Seas in water –1.5 to +2.0 °C. However, Mg/Ca values from deep Arctic and Nordic Sea environments (1000–4000 m water depth) showed an unusual and

inexplicable amount of variability apparently unrelated to temperature. They also studied downcore patterns of Mg/Ca in *K. glacialis* and discovered higher-than-modern ratios for pre-Holocene *Krithe* from several sites.

### 3. Material and methods

#### 3.1. Pliocene timeslice 3.29–2.97 Ma

We measured Mg/Ca ratios in 212 adult specimens of the deep-sea ostracode genus *Krithe* from eight DSDP and ODP sites that were used in the PRISM reconstruction of Atlantic Ocean sea-surface temperatures (SST) (Dowsett and Poore, 1991; Dowsett et al., 1994, 1996, 1999) (Fig. 1). We updated the original age model for the PRISM project (Dowsett et al., 1994, 1996) for these sites using the revised age of 3.29–2.97 Ma for the PRISM2 timeslice (Dowsett et al., 1999). PRISM2 is a global synthesis of a period of

relatively warm and stable climate lying between the transition of marine oxygen isotope stages M2/M1 and G19/G18 (Shackleton et al., 1995) in the middle part of the Gauss Normal Polarity Chron (C2An). The reconstruction spans the interval of 3.29 Ma to 2.97 Ma (Berggren et al., 1995; Shackleton et al., 1995; Lourens et al., 1996). It ranges from near the bottom of C2An1 (just above Kaena reversed polarity) to within C2An2r (Mammoth reversed polarity). It is correlated to planktonic foraminiferal zones PL3 and PL4 or *Globorotalia margaritae*–*Sphaeroidinellopsis seminulina* and *Dentoglobigerina altispira*–*Globorotalia pseudomiocenica* of Berggren (1973, 1977), and falls within calcareous nannofossil zone NN16 of Martini (1971) or CN12a of Bukry (1973, 1975).

#### 3.2. Ostracode shell cleaning and chemical analysis

The following is a brief discussion of some of the rationale for use of ostracodes as well as a description of and a rationale for the cleaning protocol employed for the samples analyzed in this study. Additional information can be found in Dwyer et al. (2002, and references therein) as well as in other papers found in Holmes and Chivas (2002). Ostracodes have several biological characteristics that make them ideal for shell geochemical studies. First, these bivalved crustaceans grow via the process of molting so that, by carrying out analyses on shells of adult specimens or other pre-adult molt stages, problems arising from ontogenetic variation in shell chemistry can be avoided. Second, ostracodes have open, chamber-free shells, which are far less susceptible to contamination by intra-shell accumulation of detrital material (the main source of contamination of Mg/Ca ratios in calcareous microfossils; e.g. Barker et al., 2003) than chambered or enclosed-shell calcareous microfossils. Third, many marine ostracode species are large (0.5 to >1.0 mm carapace length), heavy (20–200 µg), almost totally smooth and easy to clean. Single-valve analyses can be carried out routinely, and because each ostracode contains two easily separable valves, same-specimen experiments are also easily accomplished. Fourth, common marine taxa such as *Krithe*, the genus studied here, are well known taxonomically (e.g. Coles et al., 1994; Rodriguez-Lazaro and Cronin, 1999). Fifth, commonly used genera (e.g. *Krithe* and

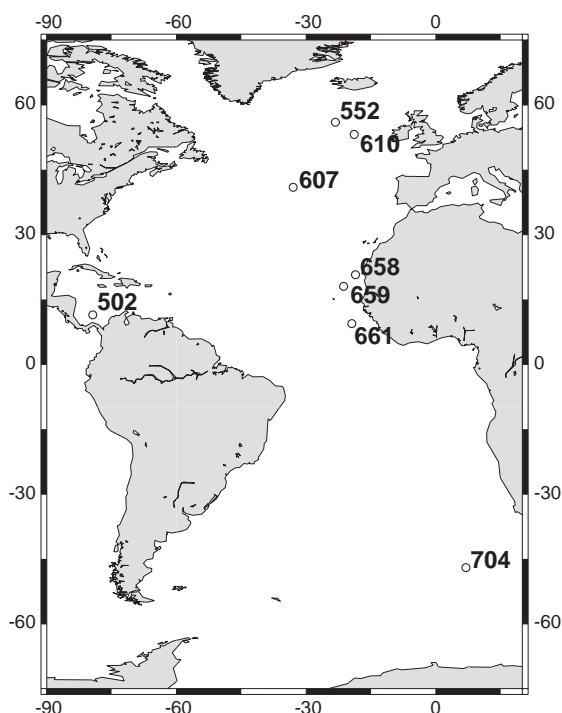


Fig. 1. Map showing Deep Sea Drilling Project and Ocean Drilling Project Sites from which Mg/Ca ratios of the ostracode *Krithe* were obtained for the interval 3.29–2.97 Ma.

*Loxococoncha*) are stratigraphically long-lived, ranging from the Cretaceous, thus providing the potential for long-term Cenozoic paleoceanography. Sixth, the ecology of marine ostracodes is becoming increasingly better known (see Holmes and Chivas, 2002). Seventh, the species of marine ostracodes most commonly used for geochemical proxy studies have relatively high concentrations of minor elements (~4 to 40 times greater than the commonly-used species of benthic or planktonic foraminifers, for example), thus further decreasing any possible impact of contamination on Mg/Ca, Sr/Ca, or Na/Ca ratios. Note that although the Mg content of the calcite in the ostracodes discussed here is relatively high, it is still well within the category traditionally referred to as “low-magnesium” calcite, and also well below the threshold that would lead to any considerable increase in solubility (see, for example, Morse and Mackenzie, 1990).

Shell cleaning and Mg/Ca analysis protocol is as follows. Sediment samples were soaked and washed in distilled water. Ostracode carapaces or valves were brush-picked from the >150 microns fraction. Species, gender, and right or left valve were recorded for most specimens. *Krithe* were identified using the taxonomy of Coles et al. (1994) and species and original authors are given in Appendix 1. Based on binocular microscopic inspection, individual valves are assigned a preservation index ranging from 1 (transparent) to 7 (opaque white) (Dwyer et al., 1995).

Each valve or carapace was soaked in commercial bleach (~5% NaOCl) for ~24 h to oxidize any remaining organic matter and assist in removal of any adhering particles. We selected this oxidizing procedure over other common treatments (e.g. H<sub>2</sub>O<sub>2</sub>, NaOH-buffered H<sub>2</sub>O<sub>2</sub>) because it is more effective at removal of shell-associated organic material (Gaffey and Bronnimann, 1993) and, unlike the other treatments, it causes no noticeable dissolution of calcium carbonate (Gaffey and Bronnimann, 1993; Pingatore et al., 1993). Furthermore, in a preliminary study to assess the effects of bleach on the elemental composition of calcite, we found no measurable difference in Mg/Ca ratios of bleach-treated and untreated samples of powdered inorganic spar calcite, suggesting that 24-h exposure to bleach does not alter the original content of Ca and Mg in calcite.

After oxidation, each shell was quadruple rinsed in deionized water, the last 2 rinses under light sonication, and dissolved in 3–30 mL of 0.05 N nitric acid, depending on shell size. Following the first 2 deionized water rinses, the shells were visually inspected at ~30× magnification and brush-cleaned of any remaining adhering particles (typically, the shells are free of any adhering particles by this stage). Routinely performed in our studies over the last decade, visual inspection of the shells prior to final rinsing, digestion, and analysis, is critical to ensure the best possible chance of contamination-free analyses. Similarly, recent work (Barker et al., 2003) has demonstrated the importance of visual inspection and removal of any contaminant particles (*after* the intensive cleaning steps) prior to final rinsing and digestion for some foraminiferal samples. The intensive cleaning developed by Boyle (1981) that is essential for studies of foraminiferal metal/Ca ratios—with multiple rigorous sonication steps designed primarily to remove the fine-grained detrital particles that typically accumulate in the chambered and ornamented shells of foraminifers—appears not to be necessary or appropriate for most ostracodes. Again, the smooth and largely pore-free shells of the most commonly analyzed species are easily cleaned of surface particulate matter by the cleaning protocol detailed above. In addition, intense sonication of the shells of many ostracode species tends to shatter the shells into very small fragments, which in turn often leads to considerable loss of material, in some cases prohibiting an analysis. Further, we have applied the intensive sonication steps for some ostracode species with highly ornamented shells (e.g. *Malzella*) that sometimes have trapped sediment in their external shell ornamentation and found no difference in Mg/Ca ratios between shells cleaned with intense sonication and shells (free of sediment to start with) cleaned by our standard protocol (Dwyer and Cronin, unpublished data). Additional evidence that the intensive cleaning is not necessary is that values for our whole-shell Mg/Ca analyses are the same as those of electron microprobe analyses of the interior portions of the shell (from shells collected from water of the same temperature, Cadot et al., 1972; Cadot and Kaesler, 1977; Dwyer et al., 2002). As



an added precaution, we routinely analyze samples for Fe, Mn, Al, K, and Ba (simultaneous with Mg, Ca, Sr, and Na) as possible proxy indicators of contamination and have not found measurable concentrations of any of these elements. While none of these are perfect proxies for any or all of the possible contaminating phases that might be encountered, lack of a detectable signal for these elements provides further support that the shells are effectively contaminant free.

Aqueous solutions were analyzed for Mg and Ca simultaneously on a Fisons Instruments Spectraspan 7 direct current plasma atomic emission spectrometer (DCP) at Duke University using matrix-matched calibration standards mixed from ultra-pure plasma-grade standard solutions (SPEX brand). Triple-acid-washed, triple-rinsed plastic labware was used throughout the procedure. Analytical precision, based on replicate analyses of samples and standards, is about 2%. Repeated analysis of a standard solution prepared from an in-house limestone standard yielded a Mg/Ca ratio of  $8.50 \pm 0.05$  (0.6% relative error,  $n=97$ ). Total procedural blanks are negligible for all elements analyzed.

### 3.3. Ostracode shell preservation

Ostracode shell preservation may be related to post-mortem processes acting on the shell that might alter the original shell chemistry. The preservation of *Krithe* shells in the present study varied from nearly completely translucent to opaque white. Dwyer et al. (1995) found only a minor correspondence between shell preservation of *Krithe* and Mg/Ca ratios and concluded that dissolution was a minor factor influencing the Mg/Ca ratios in *Krithe*. Subsequent studies confirmed that dissolution effects on shell Mg/Ca ratios in *Krithe* are minimal (Dwyer et al., 2002). Swanson and van der Lingen (1994, 1997) also presented evidence from the Tasman Sea that *Krithe* is among the most dissolution-resistant deep-sea ostracode genera. They also suggested that the intensity of ostracode shell degradation was a reflection of productivity fluctuations in surface-waters. Thus, it does not appear that dissolution alters the original composition of deep-sea *Krithe* shells to the point where it might obscure the

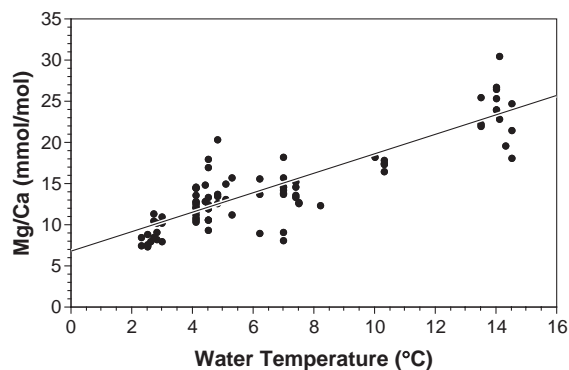


Fig. 2. Core-top calibration of Mg/Ca ratios and bottom-water temperature for adult valves of ostracode genus *Krithe* (adopted from Dwyer et al., 1995). As discussed in detail and shown graphically elsewhere (Dwyer et al., 1995, 2000), the prediction error associated with the core-top calibration is 1.3 °C for a single-shell Mg/Ca ratio. The error can be further reduced, by a factor of  $1/n^{1/2}$ , by taking the mean of Mg/Ca ratios of multiple shells (Dwyer et al., 1995).

primary patterns due to bottom water temperature (Fig. 2).

## 4. Results

### 4.1. Geographic and bathymetric variation in Mg/Ca ratios at 3.29–2.97 Ma

Fig. 3 and Table 1 show the mean Mg/Ca ratio for seven deep-sea sites plotted against the modern temperature profile for a north–south profile at 30.5°W. The mean Mg/Ca values range from a high of 10.3 mmol/mol at Site 552A to a low of 6.3 mmol/mol at Site 661A. We analyzed differences in mean values among the five sites having more than 14 specimens using a Mann–Whitney test for significance. The results revealed no significant difference between North Atlantic Sites 607 and 610A. Comparison between Site 552A and Sites 607 and 610A had a large error bar. Northern Sites (552A, 607 and 610A) are all statistically distinct from the deeper (Site 661) and the most southerly (South Atlantic Site 704) sites. Mg/Ca mean for site 704 was statistically different from those of all other sites except Site 661.

The general pattern shown in Fig. 3 is one of higher ratios in the North Atlantic at Sites 607, 610A and 552A, near the source of warm NADW, and in

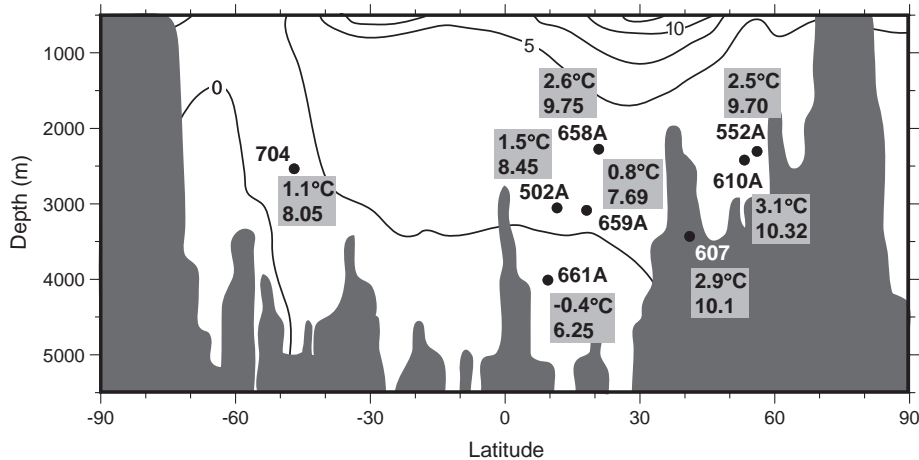


Fig. 3. Geographic and bathymetric variability in mean *Krithe* Mg/Ca ratios and estimated bottom water temperatures near 3.0 Ma obtained from seven deep-sea cores in the Atlantic Ocean plotted against modern water temperature from the World Ocean Atlas 1998, Ocean Climate Laboratory, National Oceanographic Data Center, April 1999. The bathymetric transect runs along longitude 30.5°W and core sites are projected onto this transect. Note relatively high mean Mg/Ca ratios at shallower and more northerly sites and low ratios at deeper and more southerly sites.

shallower low latitudes at Site 658A. Lower values are found in the Southern Ocean (Site 704) and the deeper low latitude North Atlantic (Sites 661A, 659A) regions influenced by colder Antarctic Bottom Water.

#### 4.2. Secular Variation 3.29–2.97 Ma

Sufficient material was available to observe secular variation in *Krithe* Mg/Ca ratios during the 3.29–2.97 Ma interval at three sites: Sites 607, 610A in the North Atlantic and Site 704 in the South Atlantic (Fig. 4). Five Mg/Ca maxima exceeding 10 mmol/mol occur at Sites 607 and 704 in the interval.

At Site 607, three of the Mg/Ca peaks exceed 11 mmol/mol. All maxima rise above the troughs in Mg/Ca values by about 2 mmol/mol and above the late Holocene value of 10 mmol/mol (Dwyer et al., 1995). These maxima in Mg/Ca ratios would signify bottom water temperatures about 1.0–1.5 °C warmer than those in the region today.

At Site 704, Mg/Ca maxima are more pronounced, reaching spikes of 13–16 mmol/mol and rising far above the baseline levels of 6–8 mmol/mol. However, these spikes represent only one or two specimens of *Krithe* and, although there is no reason to suspect that these values are spurious on the basis of carapace size,

Table 1  
DSDP and ODP site data and Mg/Ca summary

Site/Hole	Region	Latitude (°)	Longitude (°)	Water Depth	BWT-Modern	Mg/Ca analyses			Site BWT
						<i>n</i>	Mean Mg/Ca	SD	
552A	SW Rockall Plateau	56.04 N	23.23 W	2301	3	14	10.32	1.97	3.0633
607	W. Mid-Atlantic Ridge	41 N	32.96 W	3427	2.8	44	10.1	0.83	2.8754
610A	SE Rockall Plateau	53.22 N	18.89 W	2417	3.2	38	9.7	0.87	2.5338
658A	off Cap Blanc	20.75 N	18.58 W	2271	3.5	5	9.75	3.79	2.5765
659A	Cape Verde Ridge	18.08 N	21.3 W	3081	2.6	7	7.69	1.78	0.8173
661A	East Equatorial Atlantic	9.45 N	19.39 W	4006	2	9 <sup>a</sup>	8.76	0.69	1.729
502A	Caribbean	11.49 N	79.38 W	3051		10	8.45	1.36	1.4663
704	Sub-antarctic Atlantic	47 S	7 E	2532	2.4	74	8.05	2.27	1.1247
588	Lord Howe Rise	26.11 S	161.23 E	1533		4	10.65	0.85	3.3451

BWT=bottom water temperature=(854\*Mg/Ca–5.75) from Dwyer et al. (1995). Mg/Ca values in mmol/mol.

<sup>a</sup> Mg/Ca values <5 mmol/mol excluded due to suspected recrystallization (Dwyer unpublished data).

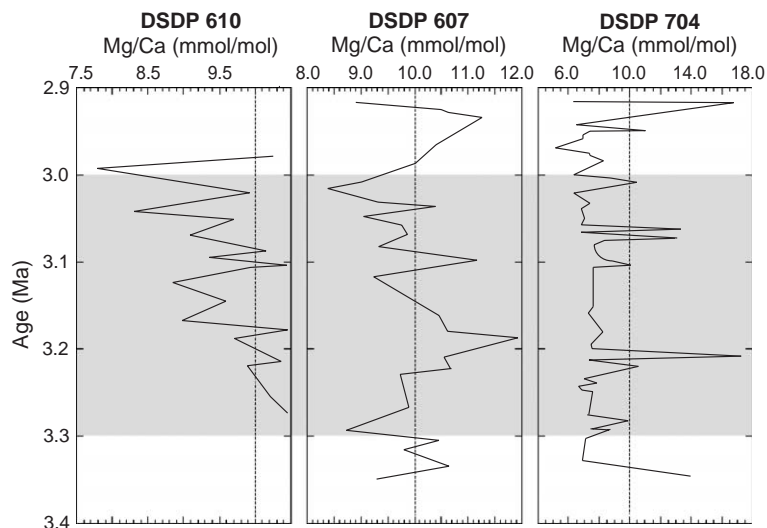


Fig. 4. Temporal variability in *Krithe* Mg/Ca ratios between 3.29 and 2.97 Ma at DSDP Sites 607 and 610 (North Atlantic Ocean) and ODP Site 704 (South Atlantic). Mg/Ca maxima at Sites 607 and 704 may represent brief, abrupt periods of warm bottom water temperatures. See text.

taxonomy, or shell preservation and cleaning, we view single shell values with extreme caution. Site 610A also revealed short-term variability in Mg/Ca ratios, superimposed on a general decrease in Mg/Ca ratios within the ~300 ky timeslab. Because the sedimentation rates and age models available for each core preclude detailed comparison of short-term events on the order of 10 ky–20 ky, or the establishment of leads and lags between the North and South Atlantic records, it remains unclear whether the Mg/Ca maxima in North and South Atlantic Oceans are synchronous. Nonetheless, the patterns of Mg/Ca variability suggest short-term bottom water temperature oscillations in the Atlantic Ocean.

## 5. Discussion

Our results can be interpreted in light of stable isotope, faunal, and floral evidence from high latitudes in the North Atlantic and Arctic Ocean which suggest that Pliocene ocean surface and atmospheric temperatures were significantly higher than those of late Quaternary interglacials (see de Vernal and Mudie, 1989; Raymo et al., 1992, 1996; Dowsett et al., 1996; Cronin et al., 1993; Edwards et al., 1991; Knies et al., 2002). Warm Pliocene surface conditions, at least in theory, might be associated with

stronger meridional overturning leading to relatively warmer deep Atlantic bottom water temperatures. Such a scenario is not suggested by the mean middle Pliocene bottom water temperature estimates presented here, which are similar to those today in the same regions.

There are several explanations that might account for simultaneous warmer-than-present high-latitude surface ocean temperatures and moderate deep bottom ostracode Mg/Ca ratios during the middle Pliocene. One reason might involve secular changes in seawater Mg/Ca ratios. Modeling and geochemical analyses of fluid inclusions in marine halite (Hardie, 1996; Stanley and Hardie, 1998; Lowenstein et al., 2001) suggest that Phanerozoic seawater Mg/Ca ratios changed significantly over long timescales. Estimates of sea water Mg/Ca ratios for early (~14 Ma) and late (~5 Ma) Neogene, Mg/Ca values were ~2.9–4.3 and ~3.3–4.8 mmol/mol, respectively, slightly lower than the modern value of 5.2 mmol/mol. Although there is no direct evidence that seawater Mg/Ca ratios were significantly lower at 3 Ma, lower seawater Mg/Ca ratios would mean that ostracode Mg/Ca ratios might slightly underestimate Pliocene deep-sea temperatures. This uncertainty would not, however, affect the Pliocene north-to-south and shallow-to-deep water BWT gradients inferred from *Krithe* ostracode shell Mg/Ca values. Higher ratios are found in shallower



and more northerly sites and lower ratios in deeper and more southerly sites suggesting bottom water temperature gradients in the Atlantic Ocean were similar to those that exist today. Billups and Schrag (2002) came to similar conclusions regarding bottom water temperature patterns reconstructed from foraminiferal Mg/Ca values for the past 27 Ma.

Another possible explanation is that mid-Pliocene high latitude oceanic and continental surface paleotemperatures are overestimated (see Raymo, 1994). This choice seems unlikely because extensive multiproxy data from pollen, planktonic foraminifers, dinoflagellates, shallow-water ostracodes and mollusks, and isotopic data from many high latitude sites are consistent with a warm Arctic and subpolar North Atlantic Ocean. An alternative explanation is that the location of Pliocene NADW formation may have been different from those regions where it forms today, i.e., the Labrador Sea and Norwegian-Greenland Seas. For example, if as suspected, the Pliocene Arctic Ocean were seasonally or at times perennially ice free (Cronin et al., 1993), then deep-water formation in the Arctic Ocean may have been a more important contributor to NADW. Under such a scenario, middle Pliocene conditions could have seen a deep North Atlantic temperature regime somewhat like today, but significantly higher sea surface temperature conditions in the North Atlantic Ocean. Mikolajewicz and Crowley (1997) suggested on the basis of modeling results that the degree of opening of the Central American Isthmus was important in influencing NADW Formation. They concluded that one impact of a partially open Isthmus would have been that the depth and location of Pliocene deep-water formation prior to about 3 Ma was different from today. Our geochemical data support these modeling results and raise the possibility that mid-Pliocene Northern Hemisphere deep water formed in more poleward locations in the Northern Hemisphere. Given that the Central American Isthmus may have opened and closed more than once during the Pliocene (Cronin and Dowsett, 1996), its history is critical to understanding Pliocene deep North Atlantic bottom temperature evolution (Haug et al., 1999). The role of altered AABW formation during the Pliocene in affecting Atlantic BWT must also be considered a possibility (Kim and Crowley, 2000).

Another factor that might have influenced NADW Formation during the Pliocene is that described by Wright and Miller (1996), who argued that another “ocean gateway”, the sill depth of the Iceland-Faroes rise, was influential in NADW formation. In theory, greater sill depth may have allowed cooler water to escape the Nordic Sea region and this could have contributed to our observed Atlantic paleotemperatures.

Finally, the inferred variability in BWT within the PRISM timeslab suggests that glacial–interglacial cycles characterized the interval, albeit of smaller amplitude than those of the Quaternary. It is quite possible that BWT during the warmest intervals of the PRISM timeslab clearly seen in the large Mg/Ca excursions exceeded those of the Holocene and indeed record strong meridional overturning. Integrated data-modeling studies underway by our group at higher resolution and greater spatial coverage (including Atlantic, Pacific, and Indian Ocean sites) will allow for further evaluation of these and other issues regarding middle Pliocene ocean and climate variability.

Regardless of the cause, the estimated middle Pliocene BWTs may have implications for models of global sea level and continental ice volume during the Pliocene because the Mg/Ca paleotemperature estimates provide a means of decoupling ice volume and temperature effects on benthic foraminiferal  $\delta^{18}\text{O}$  (Chappell and Shackleton, 1986). Dowsett and Cronin (1989) hypothesized on the basis of paleo-shorelines along the east coast of the United States that Pliocene sea level was +20 to 40 m ASL for extended periods. Kennett and Hodell (1993), however, argued that Pliocene benthic  $\delta^{18}\text{O}$  values fluctuated around a mean near late Holocene values by about 0.5 ‰ prior to ~3.4 Ma, and against significant reductions in Antarctic ice sheet volume during the Pliocene. Shackleton et al. (1995) also found that mid-Pliocene benthic  $\delta^{18}\text{O}$  fluctuated about 0.6–0.7 ‰ at Pacific Ocean site 846. Lighter Pliocene benthic  $\delta^{18}\text{O}$  likely resulted from either higher bottom water temperatures (assuming 1 °C is equivalent to 0.25 ‰, Kennett and Hodell, 1993), reduced continental ice (assuming 10 m of ice volume/sea level change is equivalent to 0.1 ‰), or both. It is open to debate whether or not the stratigraphic, geomorphological and glaciological record of Antarctica is consistent with a view of partial Antarctic deglaciation during the Pliocene (see

Denton et al., 1993; Marchant and Denton, 1996; Wilson, 1996). However, if the data presented here that Pliocene BWTs in the Atlantic were similar to those of today are confirmed through paired Mg/Ca and  $\delta^{18}\text{O}$  analyses, then a greater proportion of the benthic foraminiferal stable oxygen isotope signal for the Pliocene was probably due to reduced continental ice volume than from increased bottom water temperature.

## Acknowledgments

We are grateful to S.E. Ishman and D.A. Willard for comments on the manuscript and to Emily Klein for access to the Duke University DCP. The samples analyzed in this study were provided courtesy of Ocean Drilling Program; D.A. Hodell and D.A. Warnke kindly provided samples from ODP Site 704 samples; M.E. Raymo provided samples from Site 607. We appreciate the comments on *Krithe* shell geochemistry from P. De Deckker, H. Bauch, and K. Swanson and *Krithe* taxonomy from G. Coles and R. Whatley. M. Robinson provided graphics support. TMC and HJD were supported by the USGS Earth Surface Dynamics (ESD) Program; GSD was supported by NSF Grants ATM-0323276 (Paleoclimate) and OPP-09400250 and the USGS ESD Program, and PAB was supported by NSF Grant OPP-09400250; M. Chandler was funded by NSF Grants 0323516 (Paleoclimate) and 0214400 (Earth Systems History), and NASA's Climate Program. The paper benefited from comments from 2 anonymous reviewers.

## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.marmicro.2004.12.003](https://doi.org/10.1016/j.marmicro.2004.12.003).

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